

084915

**DISTRIBUTION
UNIT MANAGERS' MEETING
200 AREA GROUNDWATER AND SOURCE OPERABLE UNITS 0054810**

Bryan Foley..... DOE-RL RP (A5-13)
Marvin Furman DOE-RL RP (A5-13)
Ellen Mattlin DOE-RL EAP (A2-15)
Mike Thompson DOE-RL RP (A5-13)
Arlene Tortoso DOE-RL RP (H0-12)
Lisa Treichel DOE-HQ (EM-442)

Dennis Faulk.....EPA (B5-01)

Brenda Becker-Khaleel WDOE (Kennewick) (B5-18)
Zelma Maine WDOE (Kennewick) (B5-18)
Matt Mills..... WDOE (Kennewick) (B5-18)
John Price..... WDOE (Kennewick) (B5-18)
Tina Masterson-Heggen WDOE (Kennewick) (B5-18)

Jeff Armatrout BHI (H0-19)
Chloe Brewster BHI (H0-19)
Garrett Day BHI (H0-19)
Bruce Ford BHI (H0-19)
Greg Mitchem BHI (H0-21)
Joan Woolard..... BHI (H0-02)

Tim Lee..... CHI (H9-02)
Virginia Rohay CHI (H0-19)
L. Craig Swanson..... CHI (H9-02)
Mary Todd..... CHI (H9-03)
Curtis Wittreich CHI (H9-03)

Stuart Luttrell PNNL (K6-96)
Mark Sweeney PNNL (K6-81)

Administrative Record (2) BHI (H0-09)

Please inform Chloe Brewster – BHI (372-9377)
of deletions or additions to the distribution list.

RECEIVED
APR 11 2001
EDMC

Meeting Minutes Transmittal/Approval
Unit Managers' Meeting
200 Area Groundwater and Source Operable Units
3350 George Washington Way, Richland, Washington
May 2000

084915

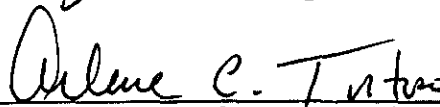
APPROVAL:


Bryan Foley, 200 Area Unit Manager, DOE/RL (A5-13)

Date

Dec 13, 2000

APPROVAL:


Arlene Tortoso, Groundwater Unit Manager, DOE/RL (H0-12)

Date

Dec. 18, 2000

APPROVAL:


Dennis Faulk, 200 Area Unit Manager, EPA (B5-01)

Date

12-20-00

APPROVAL:


John Price, 200 Area Unit Manager, Ecology (B5-18)

Date

Dec. 20, 2000

Meeting minutes are attached. Minutes are comprised of the following:

Attachment 1	--	Agenda
Attachment 2	--	Attendance Record
Attachment 3	--	200 Area UMM Minutes – May 2000
Attachment 4	--	Draft Transmittal Letter (to ER Skinnerland, Ecology) and Document "Contained-In Determination Request for Listed Waste Hydrazine (U133) at the 216-B-3 Main Pond and the 216-B-3-3 Ditch"
Attachment 5	--	Draft – Flow Chart of Data Evaluation Process for 200-CW-1 Operable Unit Remedial Investigation Report

Prepared by:

Chloe Brewster
Chloe Brewster, BHI GW/VZ Integration Project (H0-19)

Date

9/30/00

Concurrence by:

Bruce Ford
Bruce Ford, BHI GW/VZ Integration Project (H0-19)

Date

11/28/00

Please print clearly and use black ink

[illegible]

MEETING MINUTES
200 AREA GROUNDWATER AND SOURCE OPERABLE UNITS
UNIT MANAGERS' MEETING -- 200 AREA
May 25, 2000

Attendees: See Attachment #2

Agenda: See Attachment #1

Topics of Discussion:

1. 200-CW-1 Gable/B Pond and Ditches Cooling Water OU –
Work Plan Status – The work plan is on Bryan Foley's desk. He recommends moving it forward and getting it into the system. Plans on getting it out of his office by next week. It has several stops thereafter, a lot of discussion will come from it.
Status on Contained-in Determination – Mary Todd presented the drafted package (attached) and letter to E. R. Skinnarland from Bryan J. Foley (attached). Ted Wooley, Ecology, requested that the Waste Control Plan referenced in the introduction. Mary will be sending the package and letter to Bryan Foley, and it is expected to go through DOE-RL next week. Ecology should receive it by June 5, 2000.
Remedial Investigation Report – (Mary Todd) The report is in progress and headed for internal review June 5, 2000. In the beginning of July, it will go to DOE-RL, then to Ecology in August.
Data Evaluation Logic/Process – Mary Todd presented a discussion on the flow chart (attached).
2. 200-TW-1 Scavenged and 200-TW-2 Tank Waste OUs – (Mary Todd) The work plan is in Internal Review. It goes to BHI, then to DOE-RL July 7, 2000, and finally to Ecology July 18, 2000.
3. 200-UP-1 – Not discussed.
4. 200-ZP-1 – Tim Lee reported that as of yesterday, it was operating.
5. 200-ZP-2 – Virginia Rohay could not attend this meeting to report due to the Expert Panel meeting. She sent an e-mail regarding the status.
6. 200-CW-5 U Pond/Z Ditches Cooling Water OU – This OU was not discussed.
7. FY 2001-2003 Detailed Work Planning – Not discussed.
8. 200-CS-1 Chemical Sewer OU – This OU was not discussed.

Actions:

1. Reference to Waste Control Plan to be added in introduction of "Contained-in Determination Request For Listed Waste Hydrazine (U133) at the 216-B-3 Main Pond and the 216-B-3-3 Ditch. **(Action assigned to Mary Todd)**
2. Action Item List to be brought to next meeting for discussion.
3. After checking the 20X rule regarding Barium on the Summary of Characteristic Evaluation for the 216-B-3 TSD Unit, included in the Contained-in Determination Request For Listed Waste Hydrazine (U133) at the 216-B-3 Main Pond and the 216-B-3-3 Ditch, Ted Wooley will get back to Bryan Foley.

Date

Mr. E. R. Skinnarland
200 Area Section Manager
Nuclear Waste Program
Washington State Department
of Ecology
1315 West 4th Avenue
Kennewick, Washington 99336-6018

Dear Mr. Skinnarland:

Reference: Letter, "200 Area Hydrazine Contained-In Determination Strategy," E.R. Skinnarland, Ecology, to B.L. Foley, DOE, dated September 21, 1999

200 AREA HYDRAZINE CONTAINED-IN DETERMINATION REQUEST

The U.S. Department of Energy, Richland Operations Office (RL) is requesting that the Washington State Department of Ecology (Ecology) grant a contained-in determination for the listed waste hydrazine (U133) in the 216-B-3 Main Pond and the 216-B-3-3 Ditch (B Pond treatment, storage, and disposal [TSD]) soil and for 32 drums of investigation-derived waste (IDW) soil and 5 drums of IDW groundwater/purgewater associated with borehole B8758 (299-43-44) and test pits excavated at these sites. Upon approval of this request, RL will remove the U133 listed waste code from the previously generated IDW drums and will not include the code in future B Pond System contaminated soil designations. The B Pond TSD sites have been contaminated with the listed waste hydrazine from past operations as defined in Washington Administrative Code (WAC) 173-303-081(3) and are currently undergoing remedial investigation and closure planning within the 200-CW-1 Operable Unit. The referenced letter included a strategy to collect samples to support the contained-in determination and was agreed to by both RL and Ecology in a meeting held August 25, 1999.

The enclosed information is intended to meet agreements of the referenced letter. The information includes the results of soil sampling of site materials and a literature and

Internet search providing evidence of the chemical nature of hydrazine and its environmental fate. These results conclude that hydrazine is not present in the soil at levels above method detection limits (2.3 mg/kg) and would not be expected to be present based on its properties in soil. The results also conclude that the soil does not contain concentrations of Toxicity Characteristic heavy metals that would require regulation as a dangerous waste pursuant to WAC 173-303-090.

Based on this information, RL requests that Ecology grant a contained-in request for hydrazine at the 216-B-3 Main Pond and 216-B-3-3 Ditch and for the IDW drums. This request does not include groundwater associated with these waste sites.

Sincerely,

Bryan J. Foley, Project Manager
Groundwater Project

GWP:BJF

Enclosure

**CONTAINED-IN DETERMINATION REQUEST
FOR LISTED WASTE HYDRAZINE (U133)
AT THE 216-B-3 MAIN POND AND THE 216-B-3-3 DITCH**

1.0 INTRODUCTION

The following provides information to support a contained-in determination for soils contaminated with listed waste hydrazine (U133) from past operations at the 216-B-3 Main Pond and the 216-B-3-3 Ditch (hereinafter called the B Pond System) within the 200-CW-1 Operable Unit. Representative waste sites within this OU were recently investigated to define corrective actions that may be required pursuant to the *Resource Conservation and Recovery Act* (RCRA). As part of this investigation, contaminated soil was generated during characterization activities. Investigation-derived waste (IDW) from the affected sites currently have to be managed as a listed waste, increasing handling and disposal costs. Because the removal of contaminated soils is a potential remedial option under the 200 Area Implementation Plan, the listed waste issue also affects the evaluation of alternatives and the cost of remediation. Under the Land Disposal Restrictions, treatment standards for non-wastewater hydrazine waste (including hydrazine waste contained in contaminated soil) require that waste identified as U133 be treated using a specified technology regardless of concentration of the listed constituent. Specified technologies may include chemical or electrolytic oxidation, chemical reduction, or high-temperature combustion incineration (40 CFR 268.40). Currently, no onsite treatment capacity is available at the Hanford Site for the thermal treatment of contaminated soil and debris.

In accordance with Ecology's contained-in policy¹, contained-in determinations "must be based on statistically adequate site-specific data and must, at a minimum, consider the concentration and risk of each constituent for which the hazardous waste was listed and any possible breakdown products." Further, to determine that contaminated soil no longer contains dangerous waste, a demonstration that the soil does not exhibit a characteristic of dangerous waste or contain contaminant concentrations above a state-only criteria must be made. The following information and data summary are intended to fulfill these requirements.

1.1 SCOPE OF THE CONTAINED-IN DETERMINATION REQUEST

The following contained-in determination request is for removal of the hydrazine (U133) listed waste designation from the following contaminated soil:

- 32 drums of IDW contaminated soil and miscellaneous solid waste and 5 drums of groundwater/purgewater associated with borehole B8758 (well 299-43-44) drilled in the 216-B-3 Main Pond (see Table 1)

¹ Letter, T. Eaton, Ecology to All Hazardous Waste Staff, "Contained-in Policy," February 19, 1993

- contaminated soil associated with current and ongoing remedial investigations and closure planning at the B Pond System.

This request is not being extended to groundwater associated with the 200-CW-1 OU. This request is also not being extended to the 200-CS-1 OU that contains the 216-A-29 Ditch that conveyed discharges containing listed waste hydrazine to B Pond. A separate request may be submitted to Ecology in the future for the 216-A-29 Ditch.

2.0 BACKGROUND

2.1 WASTE SITE INFORMATION

An estimated total of 240,000,000,000 liters of effluent were discharged into the B Pond System. The B Pond System received mainly cooling water from all major 200 East Area facilities, but also effluents containing very low concentrations of radionuclides and/or chemicals. The use of cooling water for steam condensation and process vessel cooling resulted in the generation of very large volumes of effluent. More than 90% of all liquids discharged to the soil column in the 200 Areas were from cooling water. The pond received cooling water from the 216-B-3-1, 216-B-3-2, and 216-B-3-3 Ditches and the Plutonium/Uranium Extraction (PUREX) cooling water line as well as chemical sewer effluent from PUREX via the 216-A-29 Ditch. This latter effluent contained the listed waste hydrazine.

The B Pond was located in a natural topographic depression and varied in size from approximately 6 to 19 hectares (14 to 46 acres). This variation in size was due mainly to the pond's location in a shallow depression and fluctuations in effluent discharge. Throughout its operation, the pond varied between 0.6 m (2 ft) and 6 m (20 ft) deep. At the time the pond was decommissioned and backfilled in 1994, it had an area of approximately 14 hectares (35 acres) (DOE-RL 1993a). The 216-B-3-3 Ditch was an open and unlined earthen ditch approximately 6 m (20 ft) wide at ground level, 1.8 m (6 ft) deep, and 1,130 m (3,700 ft) long. The ditch received cooling water from B Plant via the 216-B-2-3 Ditch and associated pipeline, the PUREX cooling water line, and chemical sewer waste from PUREX by way of the 216-A-29 Ditch.

The B Pond, pursuant to the *Resource Conservation and Recovery Act* (RCRA), is an active TSD unit, although it has not received effluent since 1994. It is included on the RCRA Dangerous Waste Permit Application with the 216-B-3-3 Ditch. The B Pond System was decommissioned in 1994 by backfilling with coarse-grained material covered with vegetated finer-grained soil.

May 25, 2000

Field Characterization Activities

[illegible]

Shading indicates drum is associated with hydrazine contamination and U133 listing. Only these drums are of concern for the contained-in determination.

2.2 DANGEROUS WASTE DISCHARGES TO THE B-POND SYSTEM

PUREX chemical sewer waste discharges consisted primarily of makeup tank rinses, with lesser quantities of off-specification batches of chemicals, or overflow chemicals from tanks during aqueous makeup. Chemical solutions and dry chemicals commonly consisted of, but were not limited to, nitric, phosphoric and formic acids, sodium and aluminum nitrate, and hydrazine. Discharges regulated under RCRA were designated due to corrosivity (D002), state-only toxicity (WT01 and WT02), cadmium (D006), and hydrazine as pure chemical product (U133).

2.3 HISTORICAL HYDRAZINE DISCHARGES

Five known releases of hydrazine from the PUREX Plant between 1984 and 1986 resulted in the release of approximately 640 pounds to the 216-A-29 Ditch. In relation to the 240,000,000 cubic meters of total effluent discharged into the system, this quantity represents a negligible contribution. Table 2 provides the dates and amounts of these releases. Information on other releases was not identified.

Table 2. Known Hydrazine Releases from the PUREX Plant from mid-1983 to 1987¹

Date	Pounds
June 6, 1984	332
October 2, 1984	280
January 10, 1985	21
May 14, 1985	0.4
July 7, 1986	6
Total	639.4

¹From the 216-B-3 Pond System Closure/Postclosure Plan, DOE/RL 89-28, 1990.
Hydrazine CAS No. 302-01-2

3.0 HYDRAZINE CONTAINED-IN STRATEGY

In a letter from RL to Ecology², a strategy for obtaining a contained-in determination was identified. Within this letter, the results of a literature and internet search regarding the nature of hydrazine in the environment were provided. A summary of this information is provided in Section 3.1. In addition, a sampling strategy for verification of hydrazine concentrations in soils was identified. The strategy called for limited sampling at test pits identified in the *200-CW-1 Operable Unit RI/FS Work Plan and RCRA TSD Unit Sampling Plan* (DOE-RL/99-07). Although this sampling was completed, problems in

² Letter, B. L. Foley, RL to E.R. Skinnerland, Ecology, "200 Area Hydrazine Contained-in Determination Strategy," dated September 21, 1999.

meeting analytical holding times required a second sampling event for drummed IDW soils. The results of both sampling efforts are summarized in Section 4.0.

3.1 HYDRAZINE CHARACTERISTICS IN SOIL

Hydrazine rapidly degrades in the environment and is rarely encountered from accidental discharges into water, air, and soil. The World Health Organization indicated that the use of hydrazine in boiler water treatment might result in the brief appearance of hydrazine in waste discharge, but it would react with oxygen quickly. Hydrazine will react with dissolved oxygen at a rate inversely proportional to the concentration of the hydrazine. This source also stated that the use of hydrazine as a chemical intermediate would not likely result in its appearance in unreacted form in the environment.

The release of hydrazine to water should result in rapid degradation, especially if high concentrations of organic matter and dissolved oxygen are present. One internet source, TOXNET, estimated the half-life of hydrazine in pond water to be 8.3 days. Other sources placed the half-life of hydrazine in water from 1 to 20 days. Since discharges of hydrazine in the 200 Areas were aqueous in nature and the last known discharge of hydrazine to the environment was in 1986, hydrazine was not anticipated to be present in the 200 Area soils.

3.2 ANALYTICAL METHODOLOGY

While hydrazine in B Pond System soil is not expected, some limited sampling was conducted to provide verification. However, analysis for hydrazine in soil is not a common laboratory method based on discussions with laboratories and other research. The analytical method used was a spectrophotometric method based on American Society for Testing and Materials (ASTM) Method D 1385 (Attachment A) for testing for hydrazine in water. The ASTM method was modified based on United States Air Force (USAF) Method F33615-84-D-4400/0016. In this method, hydrazine is extracted from soil with water, which then reacts under acidic conditions with p-dimethylamino-benzaldehyde to form a stable yellow azine complex (the same procedure used in the ASTM method for the water test).

A method detection limit for this modified soil method was determined using the following analysis³. Prior to 216-B-3-3 sampling, soil samples were collected at Gable Mountain Pond (216-A-25 Ditch) for use as a medium (similar to the 216-B-3-3 Ditch) to conduct a method detection limit study for the hydrazine in soil. For the study, approximately seven samples of soil were submitted to the offsite laboratory where they were spiked with known quantities of hydrazine, then analyzed using the USAF/ASTM method. Two matrix-specific problems were encountered with this procedure: 1) the leachate became very turbid after the addition of glacial acetic acid (this turbidity was removed by filtering through a 4.5 micrometer Millipore® filter) and 2) color formation

³ Letter, C.P. Nulton, Vice President, RECRA LabNet to J. Kessner, Bechtel Hanford, Inc., *Reference: Hydrazine MDL Study*, dated October 19, 1999

was not observed with a 0.2 ppm spike to the soil samples. This is a spike level which can be easily observed in clean water and soil surrogates. This problem became apparent after the turbidity problem had been solved. Apparently some co-extracted matrix constituents were interfering with color formation. After trying several dilutions and looking at different leaching solutions, a 10-fold dilution (2 g leached with 20 mL) was used. A statistically based method detection limit of 2.3 mg/kg was derived from these analyses. Results for the detection limit study are presented in Attachment B.

4.0 SAMPLING RESULTS

4.1 FIRST SAMPLING EVENT

As stated above, holding times for hydrazine were exceeded during the first sampling event conducted on October 28, 1999. Therefore, the quality of these data were negatively impacted. Even though the holding times were exceeded by approximately 60 days, the analyses for hydrazine were performed on the samples. All hydrazine results for these samples were reported below the method detection level.

An analysis of the data collected for the B Pond system was performed to evaluate if soils are below dangerous waste designation levels. Total metal analyses were performed on soil samples collected during the investigation activities at the B Pond system, from both test pits and a borehole. Holding times were not exceeded for metals during this sampling event; therefore, the data are considered valid. A conservative 20:1 dilution was used to convert the total analysis values to toxicity characteristic leaching potential (TCLP) values (assuming 100% leaching of the constituent from the soil matrix). All sample results, with the exception of two samples for lead and one sample for mercury, showed that soils were below TCLP-regulated concentrations (WAC 173-303-090). A summary of sample results is contained in Table 3. The two samples that exceeded the 20:1 calculation for lead were rerun using the standard TCLP method⁴; these samples were analyzed within holding times. These results were below TCLP-regulated concentrations as indicated in Table 4. The sample that exceeded the 20:1 calculation for mercury was rerun for total mercury and using the standard TCLP method since this sample was outside holding times. The total indicated that the mercury had not significantly degraded. The TCLP result was well below TCLP-regulated concentrations as indicated in Table 4.

4.2 SECOND SAMPLING EVENT

Soil samples were obtained from IDW drums associated with borehole B8758 at the 216-B-3 Main Pond due to the problems associated with holding times in the first hydrazine sampling event. The analytical methodology described in Sections 3.2 and 4.1 were

⁴ Toxicity Characteristic Leaching Procedure Test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846, as incorporated by reference in WAC 173-303-110(3)(a)

followed for these samples. A total of six soil samples and one quality control soil sample were collected from six drums. In addition, one water sample was collected from a drum containing groundwater/purgewater. The results of this effort are summarized in Table 5 (results from the test pit sampling for hydrazine are also included). No hydrazine results exceeded the method detection limit determined for hydrazine in soil by the method detection limit study.

5.0 REQUEST FOR A CONTAINED-IN DETERMINATION

The Model Toxics Control Act (MTCA) Method C industrial standards for hydrazine are 43.8 mg/kg (direct exposure) and 0.0146 mg/kg (groundwater protection) in soil; the MTCA Method B standards are 0.333 mg/kg (direct exposure) and 0.00146 mg/kg (groundwater protection) in soil. Hydrazine data from both hydrazine sampling events were in all cases below the detection limit established at 2.3 mg/kg. In accordance with MTCA requirements contained in Washington Administrative Code 173-340-707(2), the practical quantitation limit for a contaminant may be used in lieu of the risk-based action level. Additionally, as identified in Section 3.1, existing information strongly supports that hydrazine would not persist in Hanford soil under the conditions in which it was discharged. Contaminated soils were also demonstrated to not exhibit a TCLP characteristic. Taking into consideration these results, RL requests that Ecology grant a contained-in determination for hydrazine (U133) in the B Pond System soil and in the IDW drums associated with borehole B8758 (299-43-44). Upon approval of this request, RL will remove the U133 listed waste code from the previously generated IDW drums and will not include the code in future B Pond System contaminated soil designations.

Table 3. Summary of Characteristic Evaluation for the 216-B-3 TSD Unit

Constituent	Maximum Concentration of Contaminants for the Toxicity Characteristic (1)	20X Rule (2)	Maximum Detected Concentration	Number of Samples	Number of Detections
VOA (ug/kg)					
1,2-Dichloroethane	0.5	10.0	ND	73	0
2-Butanone	200.0	4000.0	0.26	73	13
Benzene	0.5	10.0	0.002	73	3
Carbon tetrachloride	0.5	10.0	ND	73	0
Chlorobenzene	100.0	2000.0	ND	73	0
Chloroform	6.0	120.0	ND	73	0
Tetrachloroethene	0.7	14.0	2.1	73	3
Trichloroethene	0.5	10.0	ND	73	0
Vinyl chloride	0.2	4.0	ND	73	0
SVOA (ug/kg)					
1,4-Dichlorobenzene	7.5	150.0	ND	72	0
2,4,5-Trichlorophenol	400.0	8000.0	ND	72	0
2,4,6-Trichlorophenol	2.0	40.0	ND	72	0
2-Methylphenol (cresol, o-)	200.0	4000.0	ND	72	0
4-Methylphenol (cresol, p-)	200.0	4000.0	ND	72	0
Hexachlorobenzene	0.13	2.6	ND	72	0
Hexachlorobutadiene	0.5	10.0	ND	72	0
Pentachlorophenol	100.0	2000.0	ND	72	0
Metal (mg/kg)					
Arsenic	5.0	100.0	14.7	75	75
Barium	100.0	2000.0	119.0	75	75
Cadmium	1.0	20.0	18.0	75	53
Chromium	5.0	100.0	24.5	75	75
Hexavalent Chromium	5.0	100.0	0.43	75	1
Lead	5.0	100.0		75	75
Mercury	0.2	4.0		75	22
Selenium	1.0	20.0	1.6	75	32
Silver	5.0	100.0	9.6	75	10

Shading indicates results greater than regulatory limits; see Table 4

(1) WAC 173-303-090

(2) Conservative estimation of leachable fraction based on total results.

Table 4. Summary of TCLP Results for the 216-B-3 TSD Unit

Constituent	Sample Number	Maximum Concentration of Contaminants for the Toxicity Characteristic (mg/L)	TCLP Concentration (mg/L)
Lead	B0WKV1	5.0	0.308
	B0WKV2		0.251
Mercury	B0WKV1	0.2	0.0001

TCLP = toxicity characteristic leaching procedure

Draft
May 25, 2000

Table 5. 216-B-3 Main Pond TSD Unit Hydrazine Sampling Results

Hydrazine Sample Results from 216-B-3-3 Ditch, Test Pit BP-9			
Sample Number	Sample Depth (ft)	Concentration*	Units
B0WN01	7-8	1.0 U	mg/kg
B0WN02	7- 8 (Duplicate of B0WN01)	0.94 U	mg/kg
B0WN03	9.5-10.5	1.1 U	mg/kg
B0WN04	12-13	0.91 U	mg/kg
B0WN05	14-15	1.1 U	mg/kg
B0WN06	17.5-18.5	1.0 U	mg/kg
B0WN07	20-21	0.90 U	mg/kg
B0WN08	24-25	1.0 U	mg/kg

*Samples exceeded holding times prior to analysis.

Hydrazine Sample Results from IDW Drum Sampling, 216-B-3 Main Pond							
Drum Number	Package Date	Depth Interval (ft)	Waste Description	Samples Collected	Sample Number	Concentration	Units
600A-99-0006	9/14/1999	0-8	Soil	1	B0Y0N8	1.0 U	mg/kg
600A-99-0007	9/14/1999	8-10.5	Soil	1	B0Y0N9	0.90 U	mg/kg
600A-99-0007	9/14/1999	8-10.5	Soil	1 co-located duplicate for QC purposes	B0Y0P4 (Duplicate of B0Y0P4)	1.1 U	mg/kg
600A-99-0008	9/14/1999	10.5-16	Soil	1	B0Y0P0	0.87 U	mg/kg
600A-99-0009	9/15/1999	16-20	Soil	1	B0Y0P1	0.72 U	mg/kg
600A-99-0010	9/15/1999	20-24.5	Soil	1	B0Y0P2	0.79 U	mg/kg
600A-99-0011	9/15/1999	24.5-28	Soil	1	B0Y0P3	1.1 U	mg/kg
600A-99-0040	10/1/1999	NA	Groundwater	1	B0Y0P8	0.10 U	mg/L

U = Nondetect

Draft
May 25, 2000

Attachment A
Hydrazine Analysis Methodology



8 1997

Standard Test Method for Hydrazine in Water¹

This standard is issued under the fixed designation D 1385; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers² the colorimetric determination of hydrazine in boiler feed waters, condensates, natural, and well waters that have been treated with hydrazine (N_2H_4). This test method is usable in the range from 5.0 to 200 $\mu\text{g/L}$ (ppb) hydrazine. The range is for photometric measurements made at 458 nm in 50 mm cell. Higher concentrations of hydrazine can also be determined by taking a more diluted sample.

1.2 It is the users' responsibility to ensure the validity of this test method for untested types of waters.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific precautionary statements, see 5.3, Note, and footnote 8.*

2. Referenced Documents

2.1 ASTM Standards:

D 1066 Practice for Sampling Steam³

D 1129 Definitions of Terms Relating to Water³

D 1192 Specification for Equipment for Sampling Water and Steam³

D 1193 Specification for Reagent Water³

D 3370 Practices for Sampling Water³

E 60 Practices for Photometric Methods for Chemical Analysis of Materials⁴

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared of Spectrophotometers⁵

3. Definitions

3.1 For definitions of terms used in this test method, refer to Definitions D 1129.

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.11 on Water for Power Generation and Process Use.

Current edition approved Aug. 29, 1986. Published October 1986. Originally published as D 1385 - 67. Last previous edition D 1385 - 78(1982).⁴

² For further information on this method, the following references may be of interest: Watt, G. W., and Chrisp, J. D., "Spectrophotometric Method for the Determination of Hydrazine," *Analytic Chemistry*, Vol 24, No. 12, 1952, pp. 2006-2008, and Wood, P. R., "Determination of Maleic Hydrazide Residues in Plant and Animal Tissue," *Analytical Chemistry*, Vol 25, No. 12, 1953, pp. 1879-1883.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 03.05.

⁵ Annual Book of ASTM Standards, Vol 14.01.

4. Summary of Test Method

4.1 When a solution of p-dimethylaminobenzaldehyde, methyl alcohol and hydrochloric acid is added to hydrazine in diluted hydrochloric acid solution, a characteristic yellow color of p-dimethylaminobenzalazine is formed. The yellow color formed is proportional to the hydrazine present and in good agreement with Beer's law in the range from 5.0 to 200 $\mu\text{g/L}$ (ppb) hydrazine.

5. Significance and Use

5.1 Hydrazine is a man-made chemical and is not found in natural waters. The determination of hydrazine is usually made on boiler feedwaters, process waters, and other waters that have been treated with hydrazine (N_2H_4) for the purpose of maintaining residuals to prevent corrosion by dissolved oxygen. This reducing chemical reacts with dissolved oxygen to form nitrogen and water. However, under certain conditions it can also decompose to form ammonia and nitrogen. Hydrazine is used extensively as a preboiler treatment chemical for high-pressure boilers to scavenge small amounts of dissolved oxygen that are not removed by mechanical aeration. It has the advantage over sulfite treatment in that it does not produce any dissolved solids in the boiler water. Hydrazine is often determined in concentrations below 1 mg/L. However, in layup solutions for the protection of idle boilers, hydrazine may be present in concentrations as high as 200 mg/L.

5.2 Additionally, hydrazine provides protection to carbon steel by chemically reducing the unprotective layers of ferrous oxide (Fe_2O_3) to a more adherent protective layer of magnetite (Fe_3O_4).

5.3 Hydrazine is a suspected carcinogen and a threshold limit value in the atmosphere of 1.0 mg/L has been set by OSHA. When in an aqueous solution, hydrazine will oxidize to nitrogen and water in the presence of air over a relatively short period of time.

6. Interferences

6.1 The substances normally present in industrial waters do not interfere with the test; however, the hydrazine content may be diminished by oxidizing agents, such as chlorine, bromine, and iodine, collected with the sample or absorbed by it prior to testing.

6.2 Colors in the prescribed wavelengths also interfere. Other dark colors or turbidities that cannot be overcome.

6.3 Aromatic amines, such as aniline, will also interfere.

7. Apparatus

7.1 **Photometer**—A spectrophotometer suitable for measurements at 458 nm and capable of holding cells with a light path of 50 mm should be used. Filter photometers:

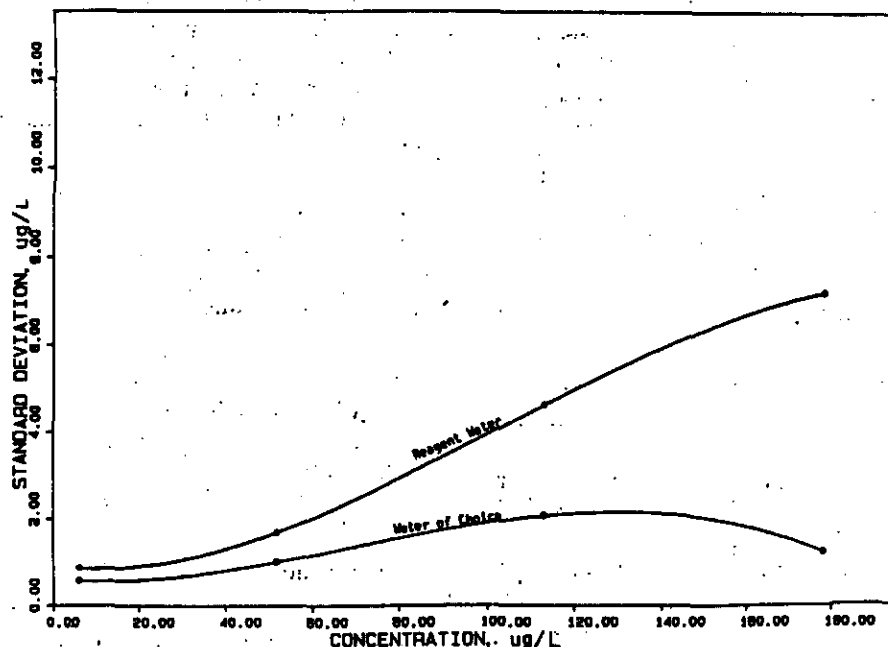


FIG. 1 Precision for Hydrazine

photometric practices prescribed in this test method shall conform to Recommended Practices E 60, and spectrophotometers to Practice E 275.

7.2 Certain photoelectric filter photometers are capable of measurement at 425 nm, but not at 458 nm. Measurements may be made at 425 nm with a reduction in sensitivity of approximately 50 % of that possible at 458 nm.

7.3 Instruments that read out in direct concentration can also be used. Manufacturer's instructions should be followed.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is sufficiently high in purity to permit its use without lessening the accuracy of the determinations.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water conforming to the requirements in Specification D 1193.

8.3 *Hydrazine Solution, Stock* (1.0 mL = 100 µg N₂H₄)—Dissolve 0.328 g of hydrazine dihydrochloride (HCl·NH₂·NH₂·HCl) in 100 mL of water and 10 mL of HCl (sp gr 1.19). Dilute with water to 1 L in a volumetric flask and mix (Warning, see Note).

8.4 *Hydrazine Solution, Standard* (1.0 mL = 0.500 µg N₂H₄)—Dilute 5.0 mL of hydrazine stock solution to 1 L

with water and mix. Prepare as needed.

Note: Warning—Hydrazine is a suspected carcinogen and should be handled with care.⁷

8.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.6 *p-Dimethylaminobenzaldehyde Solution*—Dissolve 0.4 g of p-dimethylaminobenzaldehyde [(CH₃)₂NC₆H₄CHO] in 200 mL of methyl alcohol (CH₃OH) and 20 mL of HCl (sp gr 1.19). Store in a dark bottle out of direct sunlight.

9. Sampling

9.1 Collect the sample in accordance with Practices 3370, Practice D 1066, or Specification D 1192, whichever is applicable (Warning, see Note).

9.2 Acidify and dilute the sample as soon as taken by adding 1 mL of concentrated HCl (sp gr 1.19) to a 100-mL volumetric flask and then pipetting 50 mL of the sample into the flask and diluting to 100 mL. Prepare a blank with water at the same time.

9.3 A smaller sample aliquot should be taken if the hydrazine concentration is greater than 200 µg/L.

10. Calibration

10.1 Prepare a series of standard hydrazine solutions by pipetting 0.0, 5.0, 10.0, 25.0, 50.0, 100.0, and 200.0 mL of hydrazine standard solution (1.0 mL = 0.500 µg N₂H₄) into 500-mL volumetric flasks. Add 5 mL of HCl (sp gr 1.19) to each flask and dilute with water to 500 mL and mix well. This will give standard solutions containing 0, 5.0, 10.0, 25.0, 50.0, 100, and 200 µg/L (ppb) of hydrazine.

⁶ "Reagent Chemicals. American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

⁷ MacEwen, J. D., Vernot, E. H., Haun, C. C., and Kinkead, E. B., "Chronic Inhalation Toxicity of Hydrazine: Onconogenic Effects", in cooperation with the University of California (Irvine) and the Airforce Aero Medical Research Laboratory

TABLE 1 Recovery and Bias

Amount Added, µg/L	Amount Found, µg/L	% Bias	Statistically Significant, % (95 % Confidence Level)
Reagent Water Type II			
6.041	5.891	-2.5	No
51.57	51.54	-0.1	No
177.8	178.1	0.2	No
112.9	113.2	0.3	No
Selected Water Matrices			
6.041	5.935	-1.7	No
51.57	50.77	-1.6	No
177.8	176.2	-0.9	Yes
112.9	111.2	-1.5	No

10.2 Pipet 50.0-mL portions of the hydrazine standard solutions into clean, dry 100-mL beakers or flasks and proceed as directed in 11.2. Plot absorbance on the ordinate and micrograms per litre of hydrazine on the abscissa of linear graph paper.

10.3 A separate calibration curve must be made for each photometer and a recalibration must be made if it is necessary to change the cell, lamp, or filter, or if any other alterations of instrument or reagents are made. Check the curve for each series of tests by running two or more solutions of known hydrazine concentrations.

11. Procedure

11.1 Pipet 50.0 mL of the blank, standard solutions, and acidified diluted sample solutions into clean, dry 100-mL beakers or flasks.

11.2 Add 10.0 mL of p-dimethylaminobenzaldehyde solution with a pipet to each beaker or flask and mix well.

11.3 After a minimum of 10 min, but no longer than 100 min, measure the color absorbance of each solution at 458 nm in a 50 mm cell with a spectrophotometer, using the blank as reference solution for the initial instrument setting at zero absorbance. The instrument may be calibrated with

the standard solutions to read directly in concentration if such capabilities are available.

11.4 Determine the micrograms per litre of hydrazine by referring the absorbance obtained for the sample to the calibration curve or reading hydrazine concentration directly.

12. Calculation

12.1 Calculate the concentration of hydrazine in micrograms per litre (parts per billion) in the sample by applying the following equation for the hydrazine determined in 11.4:

$$\text{hydrazine (N}_2\text{H}_4\text{), } \mu\text{g/L (ppb)} = A \cdot B / C$$

where:

A = hydrazine indicated by the calibration curve or read directly from the instrument, µg/L,

B = volume of the flask, µg/L, in which the sample was diluted in Section 9.2, mL, and

C = volume of the sample, and taken in Section 9.2, mL.

13. Precision and Bias^a

13.1 The precision of this test method was tested by seven (7) laboratories in reagent water, condensate, well water, and natural water. Three laboratories reported data from two operators. Although multiple injections were reportedly made, the report sheets that were provided allowed only for reporting single values. Thus, no single operator precision can be calculated.

13.1.1 The overall precision of this test method, within its designated range for both reagent water and selected natural water matrices, varies with the quantity tested, as shown in Fig. 1.

13.1.2 Recovery and bias data for this test method are listed in Table 1.

13.2 These data may not apply to waters of other matrices; therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

^a Supporting data for this test method are available from ASTM Headquarters. Request RR: D19-1119.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

Draft
May 25, 2000

Attachment B
Detection Limit Study Results



a division of Recra Environmental, Inc.

Virtual Laboratories Everywhere

19 October 1999

Joan Kessner
Bechtel Hanford, Inc.
2355 Stevens Drive
Building 1162
Richland, WA 99352

Reference: Hydrazine MDL Study
SAF# B99-078, SDG# H0536

Dear Ms. Kessner:

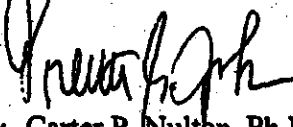
Attached is a summary of results and raw data for the referenced project. Also included is the final hydrazine method used for the MDL study and notes on the minor method modifications needed to overcome matrix problems observed in preliminary tests with the site soils.

It appears that the modified U.S. Air Force method will measure hydrazine concentrations in your soils down to approximately 2 ppm (calculated MDL = 2.3 mg/kg).

Please call me with questions and/or comments.

Sincerely,

Recra Environmental, Inc.


for Carter P. Nulton, Ph.D.
Vice President

RESULTS SUMMARY

THEORY OF CHEMISTRY

Oct-19-99 01:32pm

From-RECRA ENVIRONMENTAL INC

6102803041

T-257 OCT 19 '99 F-180 10:41AM

PARAMETER	Methods	Date	Analyst	spike ppm	1	2	3	4	5	6	7	units	Ave	SD	MDL WATER (mg/l.)	SOIL FACTOR	MDL (mg/kg)
Hydrazine (color) soil ***	Air force method	10/15/99	RDB	2.50	(0.00)	2.95	1.92	1.88	2.81	1.81	1.17	mg/kg	2.09	0.672	NA	1.0	2.3

*** For Hydrazine, sample #1 appears to have not been spiked, and has been excluded from the statistics of an outlier. The MDL is calculated from the other 6 values using the student t-factor for 6 measurements.

RAW DATA

ANALYSIS OF HYDRAZINE IN SOILS

1. Reagents (All chemical are ACS reagent grade or better)
 - 1.1 Concentrated sulfuric acid
 - 1.2 Sulfuric acid, 0.1 N
 - 1.3 Hydrazine sulfate
 - 1.4 Acetic acid, glacial
 - 1.5 Water, distilled or deionized
 - 1.6 Hydrazine reagent, p-dimethylaminobenzaldehyde (Hydraver II may be purchased from Hach Chemical Co., P.O. Box 907, Ames, IA 50010; Catalog No. 1790 or prepare a 2.5% solution of p-dimethylaminobenzaldehyde in methanol.
2. Procedure
 - 2.1 On soils, weigh out 2.0 g and add 20 mL 0.1 N H_2SO_4 . Tumble for 30 min. For water samples start here. Filter samples through 0.45 μm Millipore® and take 5 mL for analysis. Place in 25 mL volumetric flask.
 - 2.2 Add 1 mL of Hydraver II reagent or hydrazine reagent.
 - 2.3 Swirl the contents of the flasks intermittently for 8 min.
 - 2.4 Adjust flask volume to 25 mL with the glacial acetic acid reagent.
 - 2.5 Place stoppers in flask and invert bottle 5-6 times.
 - 2.6 Allow to sit for 4 min.
 - 2.7 Filter samples through 0.45 μm Millipore® using 458 nm on the spectrophotometer.
 - 2.8 Read ABS against blank using 458 nm on the spectrophotometer.
 - 2.9 Calculations, as on UDMH in soils.
3. Calibrations and Standards
 - 3.1 Weigh out 0.4060 g of hydrazine sulfate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$). Dissolve in 500

mL of 0.1 N H_2SO_4 in a 1 L volumetric flask. Bring to volume with 0.1 N H_2SO_4 . The resulting solution is 100 mg/mL in hydrazine. Prepare calibration curves using appropriate μL pipettes and the following procedure:

- 3.1.1 Make 10 ppm hydrazine sulfate daily (10 mL - 100 mg/mL to 100 mL with 0.1 N H_2SO_4).
- 3.1.2 Pipet 10 mL of 0.1 N sulfuric acid into each of six volumetric flasks.
- 3.1.3 Carefully pipet 0.05, 0.10, 0.20, 0.40 and 0.50 mL (.1, .2, .5, .8, and 1.0 ppm respectively) of the standard hydrazine solution into the flasks. Process one flask as a blank.
- 3.1.4 Add 1.0 mL of Hydraver II or hydrazine reagent to each flask.
- 3.1.5 Set time for 8 min. and swirl each flask intermittently.
- 3.1.6 After the 8-min. reaction period, bring each flask to 25 mL total volume with glacial acetic acid.
- 3.1.7 Place stoppers in flasks and invert 5-6 times.
- 3.1.8 Set timer for 4 min. to allow bubbles to disappear (tap flasks lightly).
- 3.1.9 Adjust spectrophotometer (458 nm) to 100%T using the blank solution (prepared in the same manner as the unknown samples).
- 3.1.10 Read sample or absorbance within 3 hours of Hydraver II addition.
- 3.1.11 Construct a calibration curve by plotting absorbance against total μg of hydrazine in solution.

4. References

See UDMH in Soils Analysis. USAFSAM Report TR-82-29, Field Sampling and Analysis of Hydrazine and UDMH Vapors in Air: The Firebrick Method, USAF School of Aerospace Medicine, Brooks AFB TX 78235-5501. Method modified for soil analysis by Tom Thomas, USAFOEHL, Brooks AFB TX 78235-5501.

NOTES ON MATRIX EFFECTS AND METHOD MODIFICATIONS

084915

Preliminary tests of the method as written and performed by Recra on past projects indicated two matrix specific problems. The first being that the leachate became very turbid after the addition of glacial acetic acid (Step 2.4 in the method). We found that the turbidity could be removed by filtering through a 4.5 μ m Millipore® filter (Step 2.7).

A second issue, which became apparent after the turbidity problem had been solved, was that color formation was not observed with a 0.2 ppm spike (a spike level which can be easily observed in clean water and soil samples). Apparently some co-extracted matrix constituents were interfering with color formation. After trying several dilutions and looking at different leaching solutions, we settled on a 10-fold dilution (2 g leached with 20 mL) for the MDL study.

084915

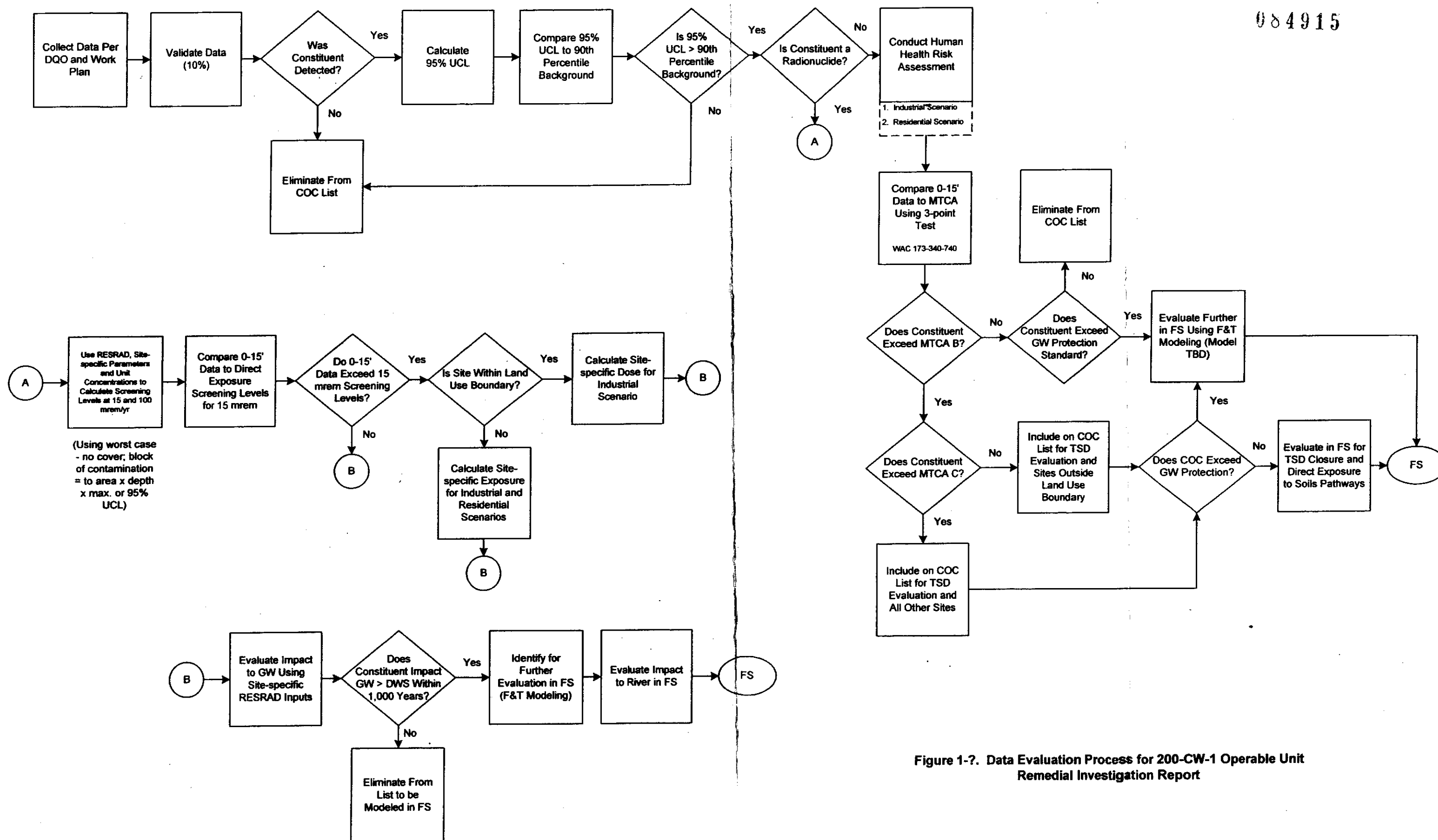


Figure 1-?. Data Evaluation Process for 200-CW-1 Operable Unit Remedial Investigation Report

DRAFT